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Distribution of Volatile Organic Hydrocarbons and Aldehydes during the IACP (Integrated Air Cancer Project) Boise, Idaho Residential Study

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16. ABSTRACT

The U.S. EPA's Integrated Air Cancer Project (IACP) conducted a field study in Boise, Idaho during November 1986 - February 1987. As part of this study, samples were collected in ten pairs of homes, one with and one without a woodburning appliance. Paired homes were located near each other and concurrent sampling was conducted inside each home and outside the home not burning wood. A different pair of homes was sampled each week during the study. Averaged data from all homes showed total non-methane organic carbon (NMOC) and total carbonyls to be higher inside either home type relative to outside. Average formaldehyde concentrations were slightly higher inside homes with woodstoves, but several non-woodburning homes had concentrations exceeding many of the woodburning homes. Benzene concentrations inside homes seemed related to mobile sources and were similar to outdoor levels.

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The U.S. EPA's Integrated Air Cancer Project (IACP) conducted a field study in Boise, Idaho during November 1986-February 1987. As part of this study, samples were collected in ten pairs of homes, with each pair consisting of one with and one without a woodburning appliance. Paired homes were located near each other and concurrent sampling was conducted inside each home and outside the home not burning wood. A different pair of homes was sampled each week during the study. Averaged data from all homes showed total non-methane organic carbon (NMOC) and total carbonyls to be higher inside either home type relative to outside. Average formaldehyde concentrations were slightly higher inside homes with woodstoves, but several non-woodburning homes had concentrations exceeding many of the woodburning homes. Benzene concentrations inside homes seemed related to mobile sources and were similar to outdoor levels.

Introduction

Between November 1986 and February 1987, the Integrated Air Cancer Project (IACP) conducted a field study in Boise, Idaho. An overview of this study has been given elsewhere (1). The residential phase of the study involved ten pairs of homes wherein one home had a wood stove (IN:WITH) and the other did not (IN:W/O). Each week samples were concurrently collected from inside one pair of homes, outside the home without the wood stove (OUTSIDE), and at three primary sites. The primary sites included a mobile source impacted site located atop a fire station in downtown Boise (FIRE), a wood smoke impacted site located in Boise's Elm Grove Park (EGP) and a background site outside Boise at an airport radio controlled air to ground station (RCAG). Samples were collected 7am-7pm and 7pm-7am on Saturday through Tuesday to observe daytime vs. nighttime and weekend vs. weekday variations.

Experimental Methods

Hydrocarbons were collected in 6 liter pacified canisters (2). Aldehydes were collected on dinitrophenyl-hydrazine (DNPH) coated silica gel cartridges (3) in duplicate. All samples flow rates were maintained using mass flow controllers.

Hydrocarbon concentrations were determined by gas chromatography with flame ionization detection. Species in the C_2-C_5 molecular weight range were separated on a packed capillary (20' x 1/16") containing Durapak n-Octane/Porasil C. Analysis of hydrocarbons in the C_5-C_{10} molecular weight range were performed on a 30 meter DB-1 fused silica column. Identities were determined through retention time comparisons and mass spectral analysis. Hydrocarbon analyses in most cases involved a composite of two canister samples representing the same time period of either a weekend or weekday sampling period; eg. Saturday and Sunday 7am-7pm were combined to make one weekend daytime sample. Typically, 0.5 liters of each sample to be combined were cryogenically trapped on a modified inlet system prior to injection.

The DNPH derivatives of carbonyl species were eluted from the sampling cartridges with 5 mL of acetonitrile and analyzed by high performance liquid chromatography (HPLC). Two C-18 columns (25 cm x 4.6 mm) in series were employed using an acetonitrile/ water gradient and detection at 360 nm. Aldehyde identities were determined by retention time comparison with standards.

Results

Table I summarizes the average values for selected hydrocarbons and aldehydes measured during the residential study. These averages represent all ten weeks of sampling and individual values range over an order of magnitude in some cases. Median values in most cases, however, were within 10% of the average values. Total carbonyls averaged between 50-60 ppb (v/v) inside homes either with or without a wood stove, while the OUTSIDE and two primary site (EGP and FIRE) concentrations averaged between 10 and 20 ppb. Background (RCAG) concentrations were on the order of 5 ppb. The distribution of the carbonyls are shown in Table II. Formaldehyde, acetone, and acetaldehyde generally accounted for 80% of all carbonyls regardless of site. All other carbonyls tended to be less than 5% of the

total.

Formaldehyde concentrations averaged 20 to 25 ppb in homes with wood stoves and 15 to 17 ppb in homes without stoves. The highest concentration of formaldehyde observed inside a home with a stove was 107 ppb while the corresponding value for a home without a stove was 33 ppb. However, concentrations were not always higher in the homes with wood stoves. Figure 1 shows the concentration of formaldehyde observed during the weekend-nighttime sampling period for all ten pairs of homes. Weeks 4,5,6 and 8 all exhibited higher concentrations in the home without a wood stove. The week 8 "in:with" home had a fireplace as opposed to a wood stove or fireplace insert which was the case in all other weeks. This home exhibited the lowest formaldehyde levels of any home in the study which were nearly the same as ambient levels. A fireplace normally has a much higher draft rate than a wood stove and could result in higher air exchange rates for such a home. However, air exchange rates were determined for all the homes in the study and were in the range of 0.4-0.7 hr^{-1}.

Figure 2 shows the formaldehyde concentrations for the sampling periods for week 7 of the study, from Saturday morning through Tuesday night. The "in:with" home that week was reported to have had a "leaky" wood stove as evidenced by wood smoke odor and elevated particulate loadings on dichot samples. Due to a rather mild winter in Boise, most wood burning activity occurred on the weekend. This correlates with the observed increased formaldehyde levels for that time period. The home without a stove evidenced more consistent formaldehyde concentrations over the entire sampling period. Outside concentrations were likewise fairly constant with the exception of Saturday and Sunday mornings. The increased levels of Sunday morning were also seen at the EGP primary site.

Table I contains the average total non-methane organic carbon (NMOC) observed for the residential study. Concentrations inside the homes were about twice the outdoor levels with notably higher levels being observed on weekend daytime samples. The higher concentrations seen at the mobile source site (FIRE) during the weekday time period may relate to increase traffic at that location. Background levels were generally quite low. Total NMOC concentrations ranged from 225 to 6721 ppb carbon (ppbC) inside homes with stoves while concentrations in homes without stoves ranged from 476 to 9493 ppbC. The very high concentrations occasionally observed inside the homes were often due to elevated levels of one or two compounds. For example, the home exhibiting total NMOC of 6721 ppbC had isobutane concentrations exceeding 4000 and 2400 ppbC during the weekend and weekday daytime sampling periods respectively. Concentrations at nighttime were an order of magnitude lower. Isobutane is used as a replacement for freon propellant in some aerosol spray cans and use of such may be an explanation for these high concentrations.

Many compounds associated with mobile sources frequently had similar concentrations both inside the homes and outside. Ethylene and benzene concentrations inside and outside the homes were similar. Isoprene concentrations, however, were much higher inside either home type than outside and may reflect that isoprene is a human metabolite. Isoprene has also been suggested as a potential tracer for tobacco smoke(4), but none of the homes involved in the study were occupied by smokers. Benzene concentrations were just slightly higher inside homes with stoves than those without. The mobile source site (FIRE) had elevated levels relative

to the other ambient sites. With the exception of the RCAG, all sites showed a similar distribution pattern for benzene. Weekday daytime levels were highest followed by weekday nighttime. Weekend nighttime concentrations were higher than weekend daytime concentrations. The benzene concentrations observed in Boise are similar to those seen in recent studies (1984-1986) of 39 U.S. urban areas (5). Median values in those studies ranged from 4.8 to 35 ppbC by site with an overall median of 12.6 ppbC.

The average toluene concentration inside either home type was about 60 ppbC while outside, EGP and FIRE sites were 19-54 ppbC. At the mobile source site (FIRE), the toluene to benzene concentration ratio held fairly constant at about 2:1. Inside the homes, however, this ratio increased to as much as 10 to one in some instances indicating some other source of toluene than mobile sources. More than half of the homes however, exhibited the same 2:1 ratio seen for the FIRE site.

Conclusions

1. Concentrations of formaldehyde and other carbonyls were higher inside homes than outside.
2. Formaldehyde concentrations were higher in homes with wood stoves on the average, but not in all cases. Activities of individuals, furnishings, etc. likely are the major factors affecting carbonyl concentrations in homes.
3. Ambient benzene concentrations in Boise were similar to those of other cities studied. Indoor benzene concentrations appeared related predominantly to mobile sources.

Disclaimer

The research described in this paper has been reviewed by the Atmospheric Sciences Research Laboratory, US EPA and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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TABLE I. Average Concentrations Observed for Selected VOC's During the Boise, Idaho IACP Residential Study[a]

	IN:WITH	IN:W/O	OUTSIDE	EGP	FIRE	RCAG
WEEKDAY-DAYTIME						
Formaldehyde	24.3	15.4	4.2	3.7	4.8	0.9
Ethylene	34.0	30.4	26.8	44.9	37.8	6.4
Isoprene	7.0	6.7	1.3	1.0	2.6	0.0
Benzene	24.4	19.7	17.3	14.6	22.5	2.1
Toluene	68.9	71.0	37.6	29.2	54.1	2.9
Total NMOC	1378.6	1002.6	523.7	480.2	803.2	132.5
Total carbonyl	52.6	57.5	10.6	9.2	11.2	4.1
WEEKDAY-NIGHTTIME						
Formaldehyde	20.7	15.2	4.9	4.4	4.7	1.1
Ethylene	31.1	28.9	26.8	52.4	40.5	6.5
Isoprene	7.2	6.6	1.3	1.6	2.3	0.0
Benzene	22.3	16.0	16.3	14.0	18.2	2.2
Toluene	57.2	63.4	32.4	25.9	42.2	3.0
Total NMOC	1009.1	878.2	494.7	461.7	688.3	112.4
Total carbonyl	51.1	50.2	12.4	11.0	15.6	4.5
WEEKEND-DAYTIME						
Formaldehyde	25.6	17.1	3.8	3.5	3.3	0.9
Ethylene	28.8	20.9	19.7	33.3	23.4	7.0
Isoprene	4.8	6.4	1.0	0.8	1.9	0.0
Benzene	18.3	13.6	11.8	10.5	13.1	2.4
Toluene	57.7	64.6	23.2	19.4	28.1	3.1
Total NMOC	1692.8	1737.1	370.0	389.5	447.1	94.8
Total carbonyl	57.4	51.9	10.1	14.4	17.3	3.8
WEEKEND-NIGHTTIME						
Formaldehyde	22.4	16.5	4.5	4.7	4.4	0.7
Ethylene	29.3	26.4	24.4	47.8	36.5	5.9
Isoprene	10.6	8.5	0.8	1.2	1.9	0.0
Benzene	19.2	15.8	14.8	13.5	15.8	2.0
Toluene	60.1	66.3	27.5	24.6	31.9	2.3
Total NMOC	936.1	1049.8	438.6	450.6	443.1	87.1
Total carbonyl	52.9	52.4	11.6	13.4	21.5	4.4

a. Formaldehyde and total carbonyl concentrations are in ppb (v/v). Hydrocarbon and total NMOC concentrations are in ppbC.

Table II. Average Percent of Total Carbonyls
Boise, Idaho IACP Residential Study

CARBONYL	IN:WITH	IN:W/O	OUTSIDE
Formaldehyde	41.8	31.9	39.2
Acetone	22.7	26.6	18.4
Acetaldehyde	18.2	20.6	20.7
Hexanaldehyde	2.8	2.8	1.0
Propionaldehyde	2.6	3.1	3.4
Butyraldehyde	2.1	6.2	3.8
Valeraldehyde	1.5	1.4	0.6
Benzaldehyde	1.3	1.2	2.0
Acrolein	1.2	1.1	1.7
Crotonaldehyde	0.4	0.2	0.5
p-Tolualdehyde	0.4	0.2	0.2
Isovaleraldehyde	0.3	0.4	0.1
m-Tolualdehyde	0.3	0.1	0.3
o-Tolualdehyde	0.2	0.0	0.0
Unknowns	4.2	4.2	8.4

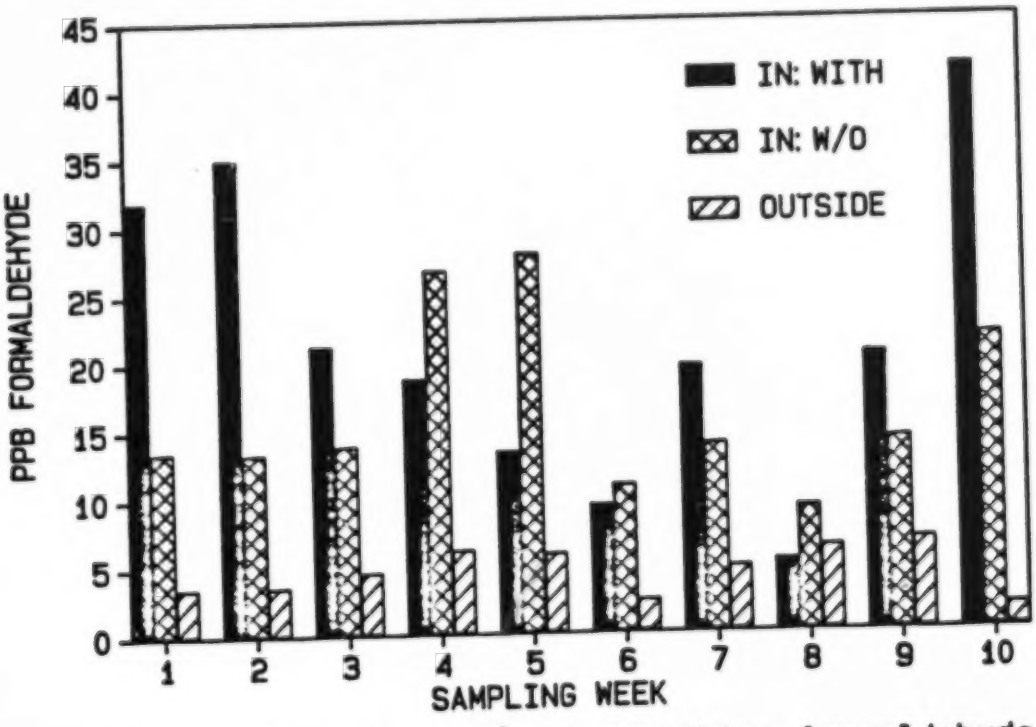

Figure 1. Average weekend nighttime formaldehyde concentrations during boise residential study

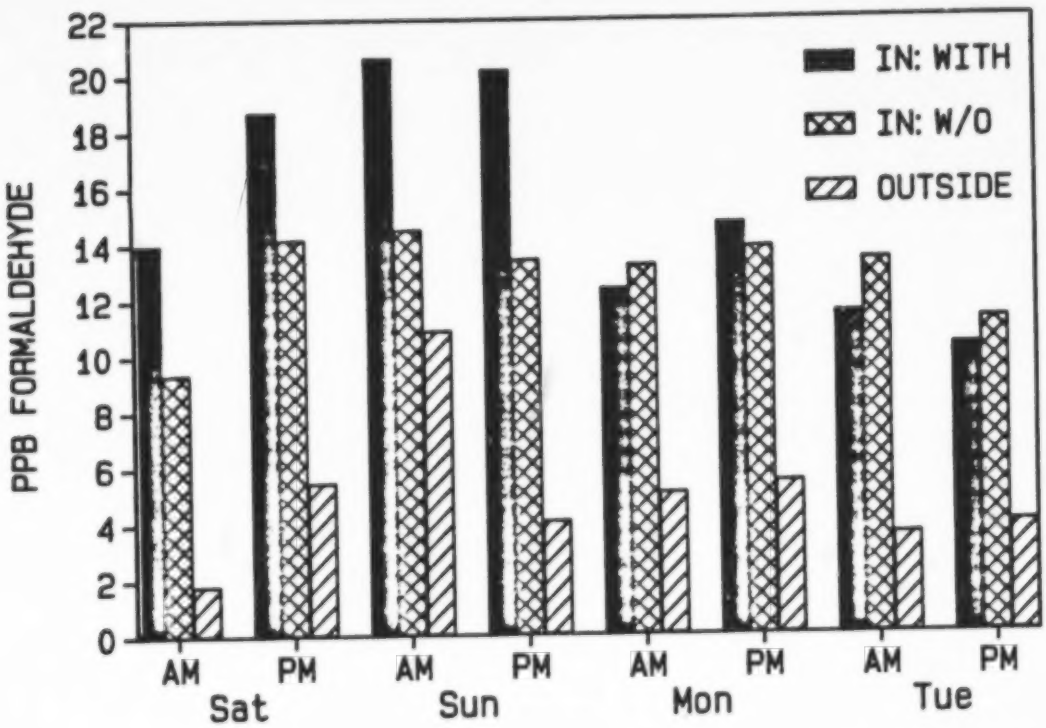

Figure 2. Formaldehyde concentrations for each sampling period of week 7; Boise residential study.